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CHAPTER 8A

Book: Safety of Lithium Batteries

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Abstract

Durability, reliability and safety are closely related in battery operation, requiring proper design to assure performance. To attain these properties are challenging and their issues of concerns need to be addressed in a coherent, holistic approach. For cell manufacturers, battery safety is about proper cell design. To implement effective safety measures, key is to engage failure mode and effect analysis in a sufficiently quantitative manner to understand cause-and-consequence relationship through advanced diagnostic and prognostic analyses to derive adequate cell design metrics to facilitate safe cell design. A key aspect of safety, not often discussed in the literature, is how to address it in the full context of electrochemical, thermal and mechanical balance. It is also important to realize that only when we can characterize the degree of tolerance and resilience to abuse, we have enough knowledge to design a safe cell and battery.

Keywords

Safety by cell design; Safety measures; Failure mode and effect analysis (FMEA); Diagnostics and prognostics; Cell balance; Electrochemical-thermal-mechanical balance; Abuse tolerance; Durability, reliability and safety

8A.1 Introduction

Lithium-ion batteries (LIBs) continue to play a significant role in energy storage and transportation applications. As performance specification becomes more demanding, the battery configuration is getting complicated as well. It is thus inevitable that battery safety issues continue to escalate as great concerns for end-users, system integrators, battery and cell manufacturers, and regulators. The concerns among the stakeholders are different in context and perspective. For end-users, the demand for a safe product is strongly guarded and should never be compromised. For system integrators safety is a critical part of the design criteria that require stringent efforts from the battery and cell manufacturers to ensure that the integrity to achieve safety should never be breached. Therefore, the cell manufacturers need to pay attention to all safety aspects of the products and pass all safety requirements, regulations and qualifications. The strategy to mitigate risks associated with safety should include the controls of the materials used, designs implemented, manufacturing quality assured and products deployed to allow the batteries to perform with the desired durability, reliability and safety.

Cell manufacturers need to address durability, reliability and safety, three essential parts of a product’s quality, with a holistic approach to ensure that a battery’s performance is in good quality. To better understand the relationships among durability, reliability and safety, from device, system to operation, Figure 8A.1 depicts the interrelationships among them. In principle, the specification defines the expectation of performance of a LIB in meeting the usage demands. The specification is supposed to be generated by the cell manufacturer together with the battery and a device manufacturer (an original equipment manufacturer or OEM who is a system integrator and uses the battery as a component) in response to market needs and consumers’ expectations.

This chapter is intended to bridge the knowledge between Chapters 7 “Lithium-secondary cell – sources of risk and their effect” and 7B “Managing of Risk by Battery Manufacturers”, so that the safety concerns from the stability issues of the materials used in the cell to the proper considerations in the battery management systems (BMS) can be adequately addressed at the cell level.

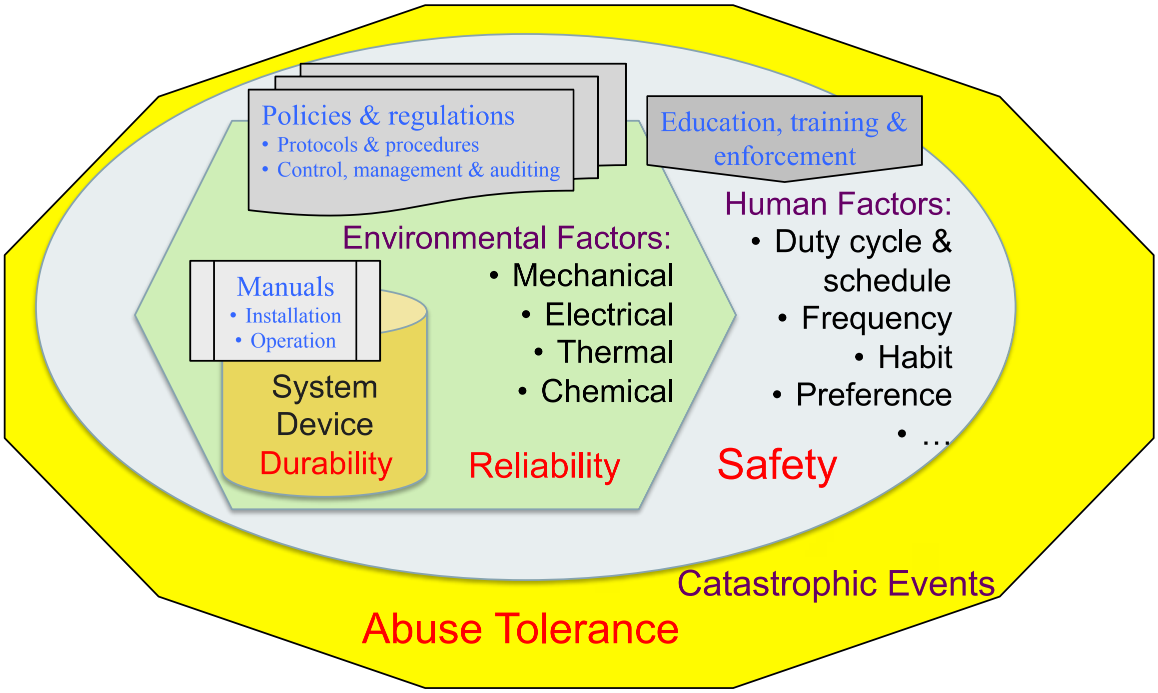


Figure 8A.1. Relationship of durability, reliability and safety in reference to abuse tolerance for a chemical system like battery.

Durability is often separated into cycle life and calendar life. However, these two characteristics interact strongly. Furthermore, the cell safety is also influenced by the aging of the cell and battery, which is discussed in Chapter 7E "Effect of electrical energy and ageing on cell safety." Durability usually is a major consideration in the battery specification and is largely determined by the materials stability and the cell design. It is a property that is often affected by other factors (from the environment and the user) that make it less predictable, introducing a significant uncertainty in expectations. This is why topics such as battery life prediction, remaining useful life, state of health, etc. become of great interests for research. However, one may soon realize that durability could be affected significantly by environmental and human factors. It is no surprise that specification of a product is usually only valid within an adequate operating environment, often confined by temperature range (thermal), humidity (chemical), altitude (mechanical), and/or electrically isolated, circuit-protected conditions to assure proper performance and reasonable durability, as expressed in the operation manuals. However, even within a controlled operating environment and condition, or sometimes slightly over such a domain unintentionally or accidentally, the impacts from the thermal, chemical, mechanical and electrical stress could have a profound, complicated and unpredictable influence on the durability of the cell or battery.

Reliability usually encounters in the assessment of durability in the consideration of such environmental and operational impacts on the performance of a cell, battery and battery-operated device. Thus, in a well-documented operating protocol and procedure, one needs to address how to control the operating environment to minimize the adverse impacts and to assure an anticipated reliability from the device/system operation. Nonetheless, human factors such as the intention of use as shown in duty schedule, personal habit or preference, inclination of care, consistency in following the protocol and procedure, etc. could further impact the durability and reliability of a cell, battery, device or system. These factors are probably the most critical aspect that ultimately determines the safety of the cell, battery, device or system. This is why education, training, and asserting disciplines are so important to the safe operation of a cell, battery, device or system.

In our view, the above description of durability, reliability and safety manifests a proper and critical understanding of a product's performance in reality. Failures and malfunctions of the product in any incidents put such reality in check. By showing the relationships of durability, reliability and safety in such a perspective, we hope the safety could be addressed more properly from components to operations. Currently, the burden of entire safety issues is placed on cell and battery manufacturers. The risk borne from the consequences of any failures or malfunctions could drive the cell or battery manufacturer to peril, simply from a recall with inevitable financial risks and reputational damages. To manage such a risk, the cell and battery manufacturers need to implement safety measures well beyond the cell design and proper manufacturing quality control.

Here the aspects of important safety measures at the cell level used by the cell manufacturers are discussed. We would like to emphasize the importance from the system level analysis to understand the failure modes and consequences, in contrast to the traditional wisdom of focusing on materials and designs. We felt strongly that through proper failure mode and effect analysis (FMEA), better strategies to mitigate safety concerns can be developed and achieved. These strategies should provide a holistic solution from materials selection to the use of peripheral devices. The intent is to provide the safety net, increase tolerance to abuse or unintentional misuse, and prevent safety incidents with redundancy in prevention measures.

8A.2 Failure mode and effect analysis (FMEA)

With regard to safety, the typical approach taken by the industry is to design, build and test the cell performance according to the specification. Design of experiments is used to derive proper parameters for cell design, scale-up and fabrication. If the design and fabrication failed the tests, the process of design, fabrication and testing will continue and through iterations to reach a product that can meet the specification. Fault tree analysis (FTA) is used to assist the iterations and understand the failure process.

It is important to recognize that cell is inherently unsafe. To meet the current design trends for portable mobile devices, with goals for high specific energy and energy density, we have to choose lightweight, highly energetic active materials tightly packed into a small volume as in LIBs. Lithium is chosen because it is a light element with a very reducing potential, both important ingredients to make high-energy batteries. However, lithium metal is inherently unstable – too reactive to most electrolytes and water to be practical in most of the LIB cell designs due to manufacturing and safety considerations. The high reactivity of lithium also introduces mechanical instability, including the problems with dendrite and pore formation, swelling, etc. during cycling. The use of carbonaceous negative electrode materials such as graphite becomes an enabling solution, since lithium can be intercalated into the graphite structure to a sufficient extent (a capacity of 370 mAh g^{-1}) with a small trade-off in available energy (with a reduction of a couple of 100 mV in voltage). This is an affordable and worthy compromise in reducing chemical reactivity and mechanical instability of lithium metal to achieve the increased usability and practicality of LIBs. Although graphite-based negative electrodes are practical for use, they still suffer from the risk of lithium plating as a safety hazard.

On the positive electrode developments, lithium intercalation in transition metal oxides with high reduction potentials is still the major pursuit for high-energy LIB designs. Along this trend of developments, pushing the capacity and potential to a higher extent continues to be the fashion. However, technical barriers remain as the electrochemical, thermal and mechanical instabilities in the cell design continue to increase safety risks.

Complicated with electrode instabilities is the stability of the electrolytes and other components (separators, binders, current collectors, etc.) used in the LIBs. The formation of solid electrolyte interphase (SEI) is the center of attention to these instability issues, which tend to result in consequences that lead to safety concerns and risks.

Besides chemical and electrochemical instability issues, thermal, mechanical and electrical instabilities during cell operation need to be considered as well. It is important to recognize that cell durability, reliability and safety issues are not only material-related but also more often design-specific. Traditionally, the design practices from material selection, electrode architecture engineering, to manufacturing process are geared to ensure the performance of the cell meets the design goals. On the other hand, to address durability, reliability and safety issues, one needs to learn from all malfunctions and failures in the system during uses and operations to identify flaws and deficiencies in the practices. The root causes of these flaws and deficiencies must be analyzed properly and can be traced back to materials quality control, electrode architecture engineering and manufacturing processes in order to correct the problems. Thus, a systematic FMEA must guide the battery design and manufacturing in order to address durability, reliability and safety issues.

In this chapter we shall address these durability, reliability and safety issues in the context of cell design and fabrication, including the understanding of properties and requirements in materials selection, electrode architecture design, cell balancing, and characteristics of abusive conditions, in order to deal with all aspects of safety-related risk management from the cell manufacturer’s perspective.

8A.3 Basic considerations of cell safety

8A.3.1Thermodynamics

8A.3.1.1 Material’s aspects

To design a cell, the first step often involves the selection of electrode active materials and other components of compositions (constituents) according to the design goals, such as energy density and power capability. For safety concerns, the stability of the constituents in the cell is the key to be considered. This aspect has been extensively discussed in Chapter 7B “Chemical reaction to risk scenarios;” yet, we shall emphasize in this chapter its relevance to cell design. There are at least four types of stability in consideration: chemical, thermal, electrical and mechanical aspects. From thermodynamic perspective, we shall start with the chemical aspect, and the subject of composition, crystal structure and phase relationship is vital in understanding the essence of safety.

We shall begin with the positive electrode materials. Currently, the most common materials are $LiFePO_4$ (LFP), $LiCO_2$ (LCO), $LiNiO_2$ (LNO), $LiMn_2O_4$ (LMO), and $Li(Ni_xCo_yMn_z)O_2$ (NCM, where x+y+z = 1). Among them, NCM has attracted more attention for its high capacity and possibly high voltage for high energy density cell designs for transportation applications (Figure 8A.2(a)). Among the different compositions, high Ni content is also favorable, due to the potential for higher voltage span and capacity performance. Depending on the compositions in x, y, and z for each transition metal content, x=y=z=0.33 is often called “333” or “111” compound. Likewise, there are other more well known compositions such as 523, 622, and 811. The higher the first digit in the composition usually indicates a higher Ni content, which is associated with higher electrode potential thus higher energy content, but it also comes with instability (with electrolyte and operation). As such, mitigation for safety measures is also more complicated. This is a quick illustration of how composition affects the chemical stability.

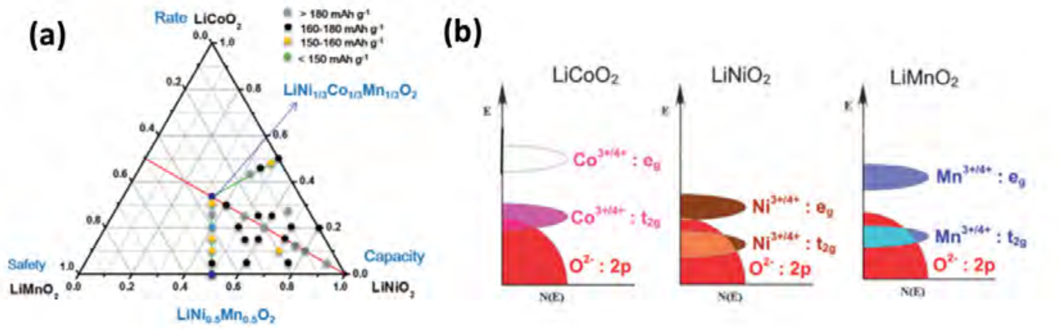


Figure 8A.2. (a) Phase diagram of Li($Ni_xCo_yMn_z$)O_2 (NCM) positive electrode compositions and (b) the electronic structures of $LiCO_2$ (LCO), $LiNiO_2$ (LNO), and $LiMn_2O_4$ (LMO) positive electrode materials [1].

Figure 8A.2(b) shows the simulated LCO, LNO and NCM energy density function (EDF) in the electronic structure of each composition, respectively [1]. As shown in these EDFs, the simulation results clearly showed how the transition metal affects the positive electrode potential and how the crystal structure influences the stability.

In terms of safety aspects, materials stability is of great concerns. Materials stability includes complicated relationships among crystal structure, mechanical, thermal, chemical and electrochemical aspects. Crystal structure stability relates to the compositional and temperature changes as depicted in the phase diagram, which in turn causes variations in electrochemical, mechanical, thermal, and chemical stabilities. It is also important to realize that crystal structure has dimensionality implications, which are related to properties such as mechanical stress and thermal and electrical (electronic and ionic) conductivities. Mechanical stability is associated with stress and strain energy distribution, as well as defect concentration and distribution, thermal gradient and distribution, and thermal expansion of the materials. Several recent review articles ([1]-[4]) are excellent references on this subject.

8A.3.1.2 Thermal stability

Thermal stability is another important property of the electrode materials. Instability usually implies that the material will decompose or change its phase. When such a process occurs, additional chemical reactions could take place, which often are unwanted. Particularly if the decomposition releases hazardous species and changes the properties of the cell. For instance, if decomposition releases gas species, the rapid increase of the pressure inside the cell could damage the mechanical integrity of the cell. Worse, gas venting could release oxygen, hydrogen, CO, alkanes or alkenes, etc., which might lead to explosion or fire, creating safety or health hazards. These types of gases emitted are described in Chapter 7C “Analysis of gases emitted in safety events.”

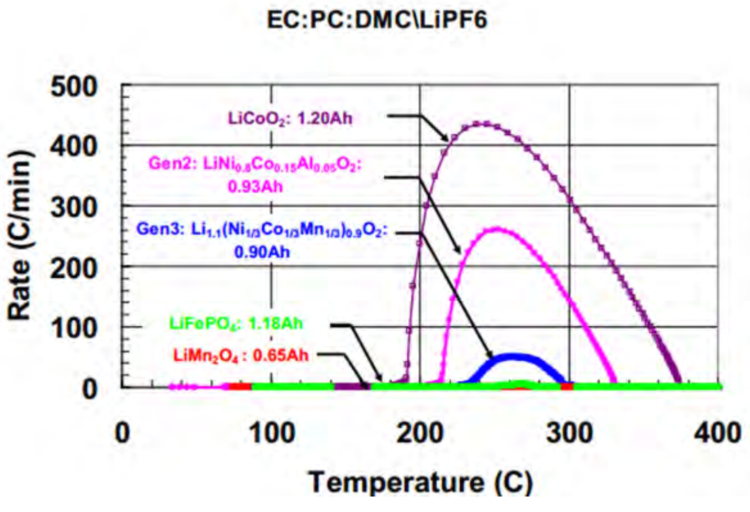


Figure 8A.3. The rate of temperature increase as a function of temperature in several well-known positive electrode materials in 18650 cells obtained by adiabatic reaction calorimeter (ARC). This representation is used to indicate the thermal stability of electrode materials [5].

Figure 8A.3 is a representation of the thermal stability of positive electrode materials used in typical 18650 LIB cells [5]. The results were obtained by adiabatic reaction calorimeter (ARC), showing the heating rate of the cell as a function of ambient temperature surrounding the cell. The results show that cells with LFP and LMO are relatively more stable than others. For high energy content NMCs, the ratio of Ni:Mn:Co also makes differences. Optimization of the composition to yield better thermal stability is certainly a factor to consider in the safety design. In principle, the results show the chemical stability of the materials in the presence of other chemicals in the cell as a function of temperature. The heat released from the cell likely represents the severity of the safety concern based on the rate of the chemical reaction and the enthalpy released from such a reaction. It is important to point out that the results do not express the detailed nature of the reactions (even though most believe that it is the oxygen from the decomposition of the active material that is reacting with the electrolyte to generate the heat) or their kinetics in terms of the factors that control the process of decomposition and heat generation. A common wisdom in the industry is to design the battery that fails safely. To design a cell that has to endure abuse in a variety of conditions and environments yet fail safely, the characterizations of the heat generation kinetics and the engineering designs to alleviate the thermal effects internally (in contrast to the thermal management externally, as explained in Chapter 8B “Managing of risk by battery manufacturers”) are very critical steps to master.

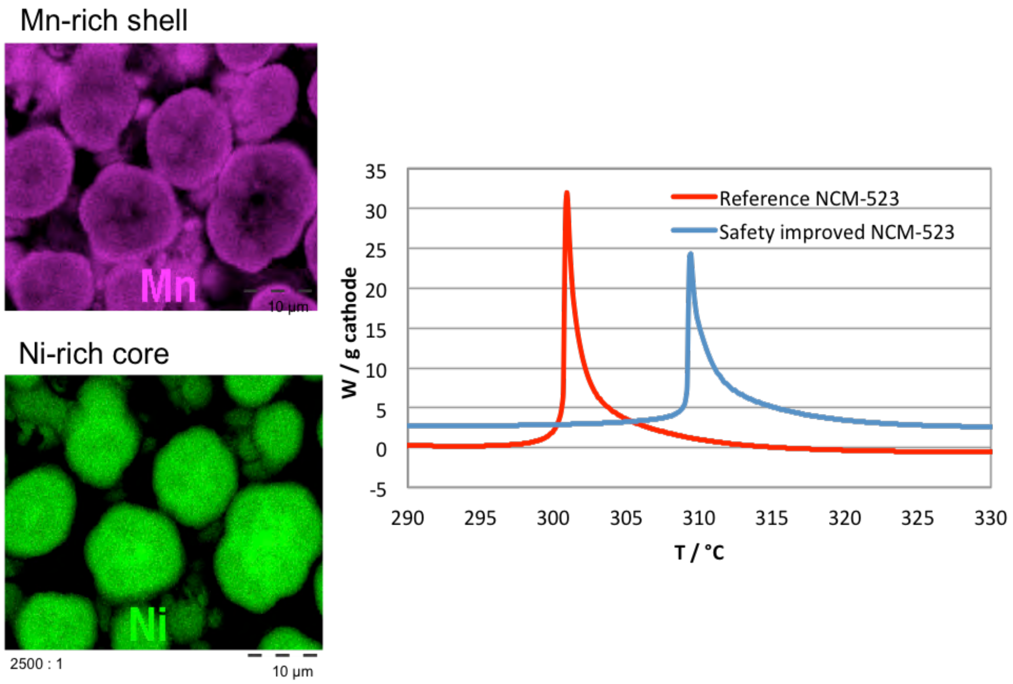


Figure 8A.4. (a) Elemental Mn and Ni distribution on the surface and core of a core-shell NCM positive electrode material. (b) The DSC results show the surface-Mn-rich core-shell material has better thermal stability than the conventional NCM-523 material [6].

Figure 8A.4(a) is a micrograph obtained from scanning electron microscopy (SEM) with an energy dispersive spectroscopy (EDS) analysis to show the elemental Mn distribution on the surface and the Ni content in the core of a surface-Mn-rich core-shell NCM-523 material [6] used in a cell design. With such a core-shell microstructure in the particle, the material showed a better thermal stability than the conventional NCM-523 composition, as indicated by the differential scanning calorimetry (DSC) results in Figure 8A.4(b), in which the core-shell material exhibits a higher decomposition temperature.

8A.3.1.3 Electrode architecture, design and fabrication

Although material's stability is a prerequisite for a safe cell design, electrode architecture, design and fabrication are probably more critical for a cell's resilience toward abuse in the safety design than material's intrinsic stability. This is exemplified by the facts that, although LFP is considered a safe material, some LFP cells could be designed to fail safely, while others still exhibit safety hazards when they are abused. The key message is that the electrode architecture and design strongly affect the rate capability and electrode kinetics in a cell. To properly mitigate heat generation and dissipation is equally critical to high power and high energy density in the cell design.

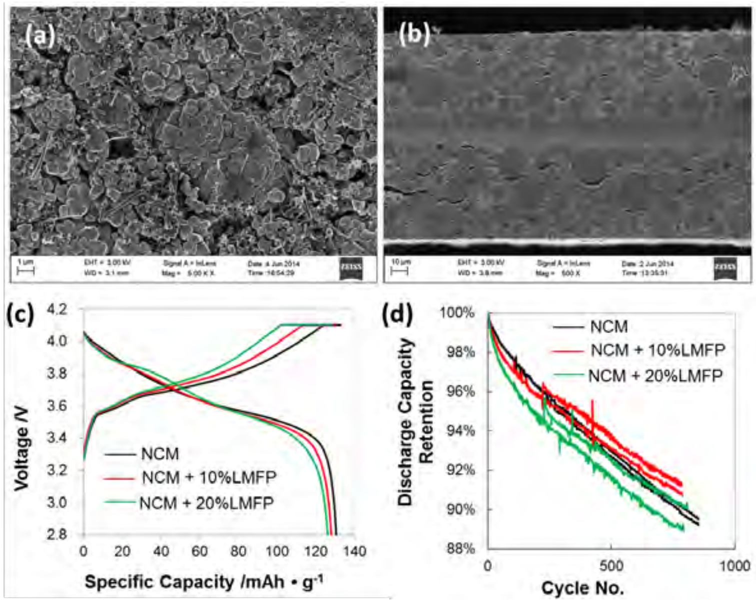


Figure 8A.5. An example showing that mixing NCM with a thermally more stable $LiMn_xFe_yPO_4$ (LMFP) composition in the positive electrode could improve its safety aspect without sacrificing electrochemical performance. The SEM micrographs show (a) the electrode surface morphology (b) the cross section of the electrode architecture. (c) Charging and discharging profiles and (d) charge retention in cycle performance for the NCM base material and the NCM+LMFP composites.

Figure 8A.5 shows an example regarding how thermal stability of an electrode can be engineered. Here, a composite electrode made of a typical NCM material mixed with thermally more stable $LiMn_xFe_yPO_4$ (LMFP) in the composition is used as an example. The results indicate that cell performance could be retained while better thermal stability achieved. Figure 8A.5(a) and (b) display the SEM micrographs of the surface morphology and cross section of the electrode architecture of the mixed composition. The SEM examinations show that a homogeneous particle distribution of the composite electrode could be achieved in the fabrication. Figure 8A.5(c) and (d) show that the charge and discharge profiles of various compositions exhibit similar capacity and charge retention in the cycle performance. This example depicts the spirit of electrode engineering where, with careful design and optimization, safety aspects could be improved through smart electrode architecture design and fabrication to preserve cell performance.

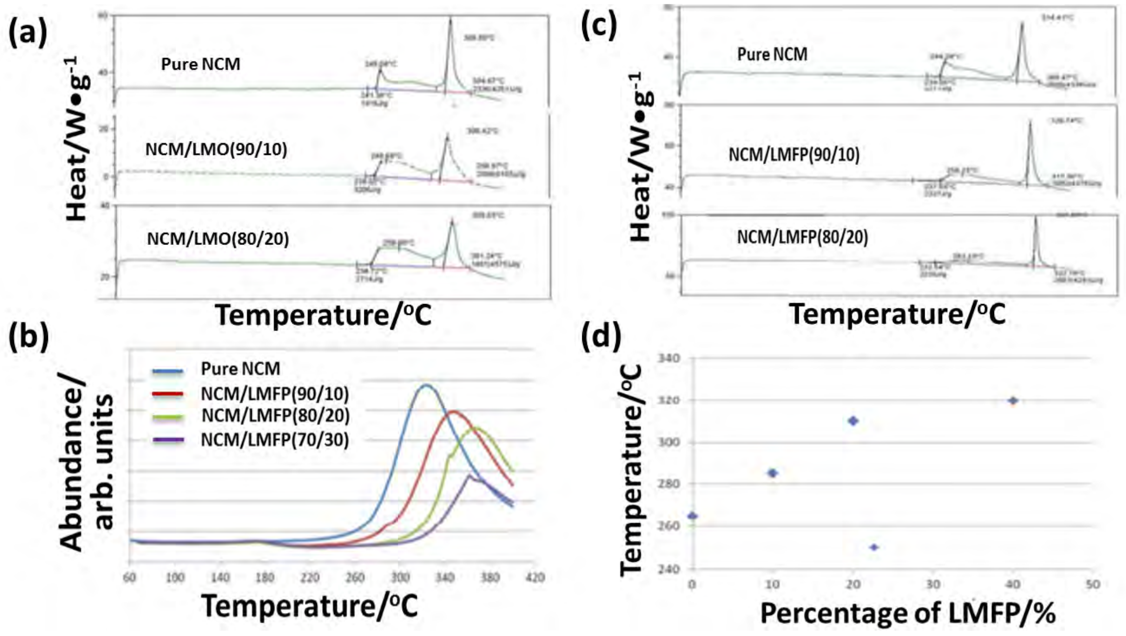


Figure 8A.6. DSC results show the composite electrodes of (a) NCM+LMO and (b) NCM+LiMn$_x$Fe$_y$PO$_4$ (LMFP) could exhibit better thermal stability than the base NCM material. (c) The amount of oxygen released in several compositions of NCM+LMO samples. (d) The temperature of oxygen release as a function of LMO content in the composition [7].

Figure 8A.6 is another example of thermal stability improvement by the composite electrode approach [7]. Here DSC results for (a) NCM+LMO and (b) NCM+LMFP, each with three variations in composition, were compared. The thermal signature of the composites indicates that the blends with higher ratios of LMO or LMFP release less heat, as exhibited by the reduced intensity of the DSC peaks, although the decomposition or phase transition temperatures stay roughly the same. However, in the composites of NCM+LMFP, Figure 8A.6(c) and (d) show that the amount of oxygen release (from mass spectra) could be reduced and the temperature of oxygen release deferred with higher ratios of LMFP. These examples illustrate the mitigation of the heat and oxygen releases and the increase of the temperature for the oxygen release in the positive electrode active materials that can improve safety features.

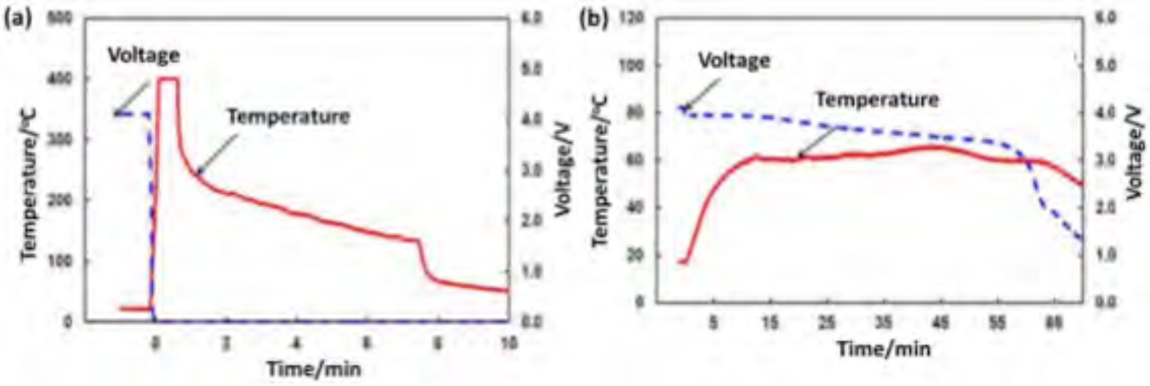


Figure 8A.7. Results of nail penetration experiments with cells made of (a) graphite || NCM and (b) graphite || NCM+LMFP. In each figure, the dash lines are cell voltage and solid lines are cell temperature [7].

Figure 8A.7 shows the results of the safety engineering strategy mitigated by the NCM+LMFP composite as demonstrated by the nail penetration tests using (a) graphite || NCM and (b) graphite || NCM+LMFP cells in the experiments [7]. Using a typical graphite || NCM cell the nail penetration immediately resulted in short as indicated by the rapid drop of the cell voltage to 0 V, while the cell temperature quickly raised to over 400°C. The short however did not cause thermal runaway and the cell temperature dropped gradually to fail safely. In contrast, with a graphite || NCM+LMFP cell, the nail penetration did not result in short, but a continuous discharge, as shown by the cell voltage profile; and the temperature of the cell raised to 60°C initially yet remained in the vicinity of that temperature over the course of the discharge. This example demonstrates the success in mitigating the thermal hazard by engineering active material composition and the electrode architecture. By blending LMFP in the positive electrode composition, the higher thermal stability of the LMFP reduces the heat and oxygen releases and decreases the likelihood of thermal runaway, increasing resilience to abuse.

8A.3.1.4 Cell balance

In addition to the considerations of materials stability, electrode architecture design and process engineering, the cell balance is also very important to the cell's ability to provide additional tolerance to abuse and resilience for safety. Cell balance includes mass balance, capacity balance, rate balance, and thermal-mechanical energy balance. As indicated earlier in the concept, such balance is critical to the health of the cell. Most of the cell balance designs focus on capacity/charge balance in a cell. This capacity/charge balance often refers to the loading ratio of the negative electrode against the positive. Rate balance is less discussed in the literature. The goal is to minimize polarization in each electrode, so the impedance of the cell can be reduced, whereas no one electrode is subject to significant stress under normal operation within the performance envelope. For the negative electrode, this is particularly true to prevent lithium plating.

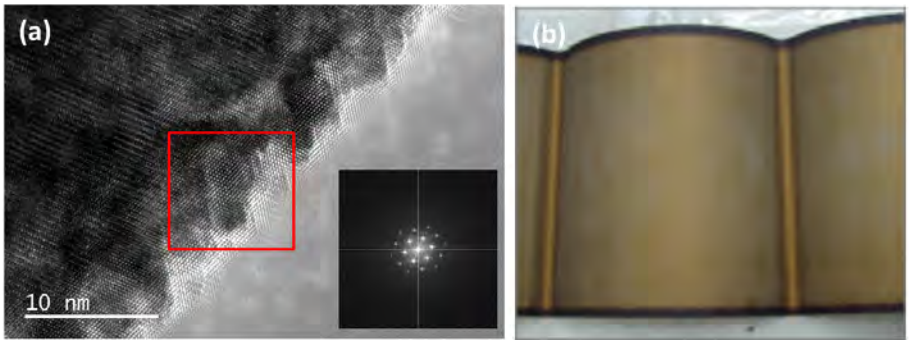


Figure 8A.8. (a) TEM image showing the surface crystal structure changes in a cell with graphite || NCM under a condition of cell over-balance (negative electrode is more than desired). (b) Lithium plating shown on the negative electrode due to cell under-balance (negative electrode is less than desired).

Figure 8A.8 shows two examples about the importance of cell balance. In the first example, a graphite || NCM cell was used to illustrate the effect of an excessive cell balance (over-balance) situation that results in degradation in the positive electrode. When the cell is over-balanced, thus the negative electrode is more than desired; the extent of the first staging plateau at the negative electrode in the cell balance could be less utilized. The rate of loss of lithium inventory could thus increase, resulting in a higher slippage in the capacity balance between the two electrodes. As a consequence, the negative electrode potential might come sooner to rest on a higher potential range toward the second staging plateau, so the cell might experience degradation due to overcharging (i.e. excessive de-intercalation of lithium) in the positive electrode that causes oxygen release and localized crystal structure changes near the surface of the NCM composition, as shown by the high-resolution transmission electron microscope (TEM) imaging in Figure 8A.8(a) where spinel-like phase was identified. The second example (b) shows a case where insufficient cell balance (under-balance) in a cell led to lithium plating on the graphite negative electrode, which could further lead to more consumption of electrolyte as a result of electrolyte decomposition and SEI formation, reduced cycle life, and increased propensity of creating safety hazards.

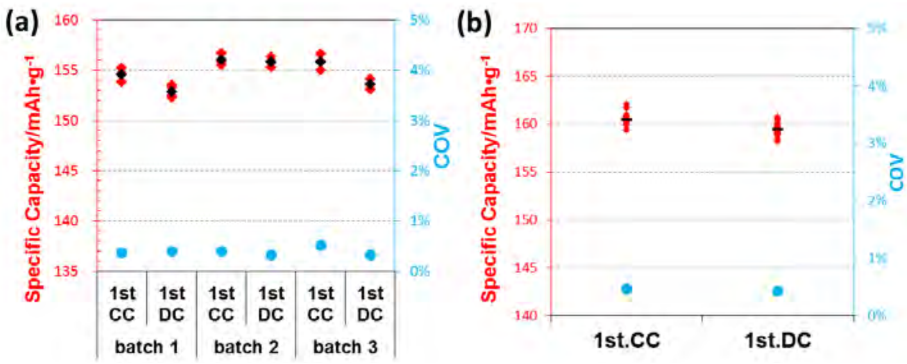


Figure 8A.9. Distribution of capacity (a) among graphite || LFP cells of different lots that use various batches of LFP material and (b) among different LFP electrodes in similar cells of the same batch. [COV: Coefficient of Variation]

Cell balance could be generated not only by design attributes but also from the quality of the manufacturing process control. Such control measures include quality of the raw materials obtained from the vendors in terms of batch-to-batch variations, process condition control in each fabrication steps, precision and consistency of the equipment and tool in the manufacturing process, production schedule, variations in human handling and many other factors. To some degree, even the homogeneity of the electrode could be a concern, since such subtlety is often difficult to detect properly and put into control measures.

Figure 8A.9 shows two examples of such subtleties in controlling cell balance in the cell manufacturing. In the first case (a), a nominal graphite || LFP cell design was used to illustrate the variations in the capacity of the LFP electrode in coin cells that use different batches of LFP raw material. Even with tight control of the procedures used in the fabrication, such capacity variations are quite common yet different from batch to batch. In case (b), the variations among different locations in the electrode roll that were made into cells (from the same batch of the LFP raw material) are still detectable.

8A.3.1.5 Aging and degradation

It is vital to build in safety measures in cells through proper design and engineering, consistent manufacturing quality control, and high precision process to fabricate reliable cells. Nonetheless, a large range of variations and uncertainty in safety measures actually come from battery use. The traditional wisdom to deal with this difficulty is commonly handled through proper battery management. It is inevitable that battery ages and degrades in its life. What makes it difficult to handle is the fact that the degree of degradation and its variations are sensitive to the operation conditions, schedules, and other factors that are often hard to control (referring to Figure 8A.1). It is also common that the spread of the variations widens as the battery ages. How to address safety issues could become difficult to quantify.

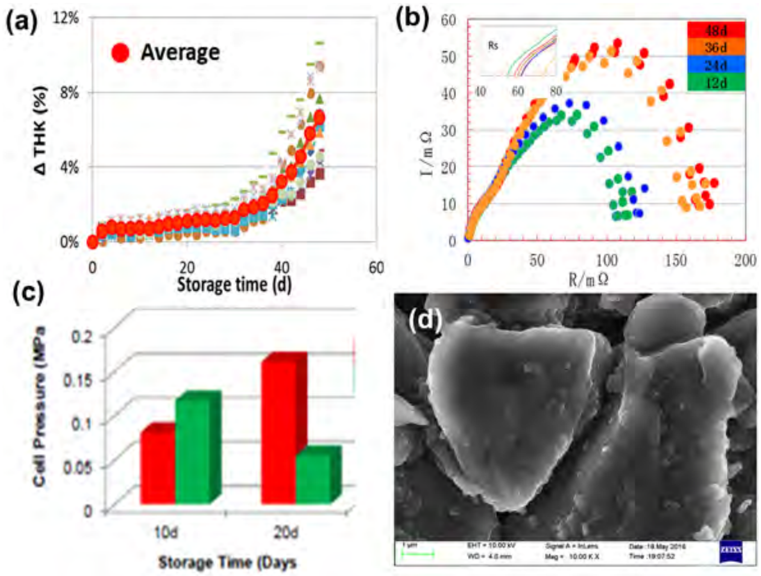


Figure 8A.10. The (a) thickness, (b) ac impedance, (c) internal pressure of the cell, and (d) surface morphology changes of the positive electrode in nominal graphite || NCM cells that undergo calendar aging at an elevated temperature.

Figure 8A.10 displays observations in a few measurable or observable metrics that describe the cell aging behavior for a nominal batch of graphite || NCM pouch cells that underwent calendar-aging tests at 60°C in a hot box. In general, the calendar aging in a hot box will age the cells in a more aggressive manner by thermal stress. The consumption of the electrolyte should be higher. The growth of the SEI would be more severe (Figure 8A.10(d)). Figure 8A.10(a) shows that the thickness of the cells (swelling) increases with the aging period, as well as the spread of the variations. Figure 8A.10(b) shows that the impedance of the cells increases as well, including the variations among the cells. Figure 8A.10(c) indicates the internal pressure (likely from the gassing) of the cells varies with calendar aging. These phenomena as observed and measured show a complex nature of aging and possible consequences toward safety. The general belief is that these changes could have some severe consequences. For example, cell swelling may reflect changes in the mechanical property of the cell, including phenomena caused by gassing, disintegration of the particles in the electrodes, or deformation of certain components in the cell; thus, cell mechanical stability might be compromised. However, what exactly is compromised might not be easy to identify for safety and risk assessment. If a confined containment for the cell is encountered, the swelling could raise immediate concerns for compression-led internal shorts. Swelling could also lead to degradation in performance if it is due to delamination of the electrode that could cause overcharging or discharging, higher heat generation caused by worse contact and higher resistance, or uneven reactions and rates in electrochemical behavior. Impedance increase in general signals a less effective reaction in the cell and more heat generation. A secondary effect is localization resulted from inhomogeneity in the current or voltage distribution. This is also true for gassing and internal pressure increase in the cell that has consequences in degrading cell mechanical integrity and varying electrical energy distribution that could lead to effects in the local scales and trigger safety events. These variations presented in the chemical, mechanical, electrical and subsequent thermal energy balance are difficult to predict, prevent, and mitigate. A better characterization and quantification protocol needs to be developed in the future to allow a better battery management.

As we conclude the section on thermodynamics and stability issues with cells that can impact battery safety, one important take-away is that many possible incidents like what we discussed so far are “single point failures” that are difficult to detect and manage. Fortunately, with careful design considerations and mitigation strategies, the probability of occurrence of these single point failures is sufficiently low to date. However, with increasing complexity in functionality and market demand for high-energy high-power designs, options for better safety design and mitigation are reducing and more constrained day by day.

8A.3.2Kinetics

8A.3.2.1 Kinetic effects during polarization

Although the thermodynamic aspects such as various types of cell stability discussed above are critical in cell performance, in reality the cell performance is largely determined by the kinetics of the cell during polarization. During operation of a battery, the polarization and the associated kinetic effects are a dominant factor in leading to the likelihood of a safety event. The kinetic aspects are also the most difficult ones to deal with, due to the lack of methodologies to assess the effects that can cause safety events. Here we shall describe the essence of these concerns.

Cell kinetics is often determined by the electrode architecture and morphological variations in the processing, particularly in the formation, which complicates the kinetic assessment. Referring to the earlier discussions on cell balance, in the thermodynamic aspect, it is often related to the electrode loading and capacity matching to ensure proper charging and discharging mechanism can be followed. In the sense of kinetics, the cell balance also needs to address the rate capability matching between the two electrodes. This rate capability balance between the two electrodes is very difficult to achieve and assess as cell formed and aged. Due to cell formation and subsequent aging, the electrode morphology, including porosity and tortuosity, may change substantially. It is often difficult to assess how much changes had happened and their impacts on cell kinetics. Although cell swelling, other form factor variations and impedance changes could be measured, the degree of rate capability mismatch between the two electrodes is often to be determined. Such a mismatch could induce events such as lithium plating and other safety concerns. Thus, in addition to the volume expansion and material’s stability issues, the root causes of cell kinetics imbalance are rather important since they touches the balance of chemical, electrical and mechanical aspects in the cell design and subsequent effects on safety concerns.

In Figure 8A.11 we present a case study on kinetics-induced instability, where electrode design and architecture is critically related to the active material’s stability, and sophisticated engineering would be required to develop a reliable structure to sustain the cell operation through cycling. In this case, the NCM particles upon hydraulic compression and cycling continue to develop cracks, as observed by the SEM examinations. This process continues to create new particle surfaces, change inter-particle contacts, modify pore structure, porosity and tortuosity, affect SEI formation and growth, and create swelling that changes the stress and strain field of the inter-particle interaction and electrode shape and thickness; all could alter electrode kinetics and rate capability. The subsequent effects on cell durability, reliability and safety would be difficult to identify and quantify.

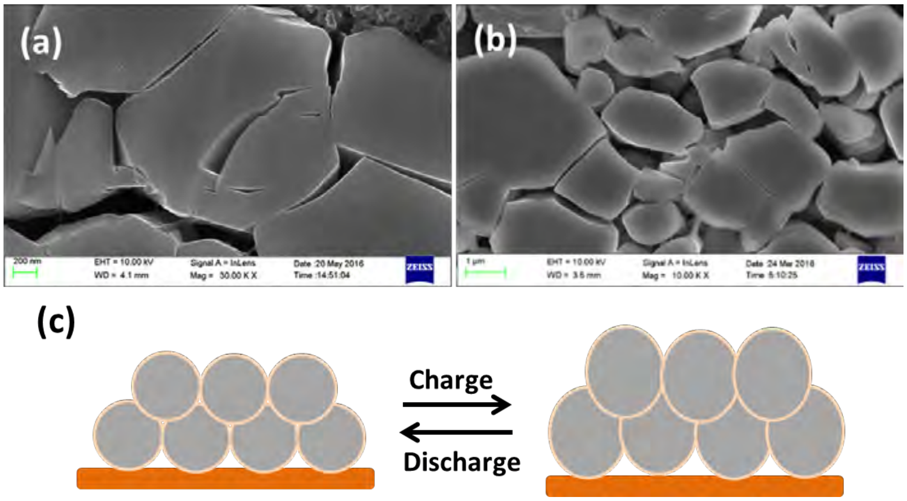


Figure 8A.11. Electrode architecture and materials stability demonstrated by an NCM-based electrode design and architecture. Micrographs of the NCM electrode: (a) after the cold press and (b) after cycling for comparison. (c) Graphical mechanistic explanation of the particle pulverization leading to swelling of the electrode upon cycling.

Taking nominal graphite || NCM cells as examples, Figure 8A.12 shows the effects of kinetics on cell behavior. In Figure (a), the charging profiles at various rates are shown, illustrating the capacity of the constant current charge regime from a fully discharged state to the cut off voltage before the constant voltage regime as a function of charge rate. Figure (b) exhibits the cell surface temperature as a function of the charge input under these charging practices. In Figure (c), the extent of lithium plating on the negative electrode surface from the charging process is shown. Although the amount of the lithium plating on the negative electrode cannot be readily derived or measured, the visual comparison does give some degree of knowledge of the issue and the propensity of the risk with safety issues. In general, the higher the rate, the more the cell temperature rise, the greater extent of the side reactions that consume the electrolyte, the worse the cell balance and the higher possibility of lithium plating. All contribute to the safety hazards.

There are other mitigation methods to deal with kinetic issues regarding a material's stability. Strategies such as designing core-shell microstructures for the active materials, using surface coatings, employing redox shuttles to protect overcharging or overdischarging, have been reported in the literature. As for the electrolytes, non-flammable compositions, retardants, additives are often being considered. Chemical and thermal analytical techniques, such as ARC, DSC, TGA/DTA, gas analysis, and ICP to analyze metal dissolutions, are also used for proper characterizations of the effectiveness of the strategies.

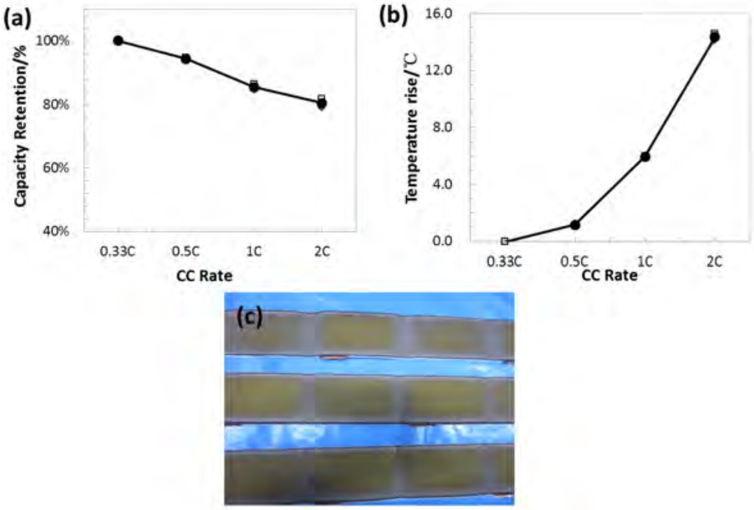


Figure 8A.12. (a) The charging profiles of a nominal graphite || NCM cell under charging at different rates. (b) The cell surface temperature variations and (c) the visual evidence of Li plating on the surface of the negative electrode.

8A.3.2.2 Electrode design and architecture to reduce polarization

To minimize the kinetic effects and side reactions, the principal effort in cell design is to minimize cell polarization. This is often achieved by proper electrode design and architecture. Figure 8A.13 shows an example using two binders and their effects on electrode polarization as an illustration. Here negative electrodes with two different kinds of binders in a typical graphite matrix are demonstrated. In Figure (a), the Nyquist plot of the impedance spectra is shown to depict the differences in kinetics the electrodes of the two binders exhibit. The details the binders impact the electrode polarization in performance are shown in Figure (b) where the attributes in the impedance spectra were analyzed and compared.

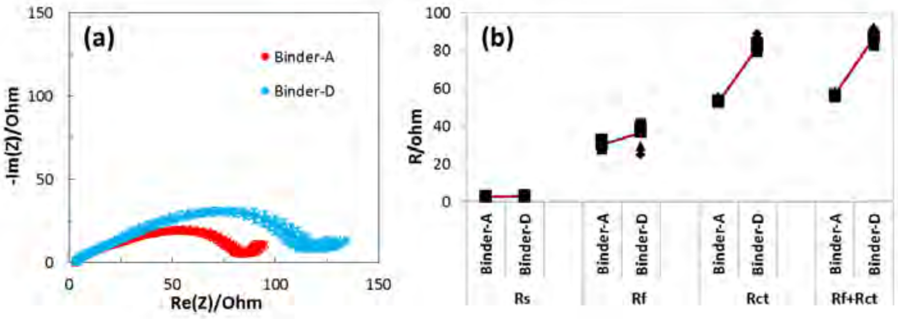


Figure 8A.13. (a) The ac impedance of graphite negative electrodes prepared with different binders. (b) Different attributes to the cell impedance were analyzed for comparison of the impacts from the binders. The experiments were performed at 25°C with a symmetric cell configuration.

The attributes in the electrochemical impedance spectra can be analyzed by equivalent circuit diagram and model parameter fitting. These attributes are categorized into (1) R_s – a resistance that represents the serial contact resistance, (2) R_f – representing the porous media transport resistance, and (3) R_{ct} – responsible for the charge transfer process. These values were determined by a symmetric cell configuration in which the same negative electrode matrices and compositions were used for electrochemical impedance measurements at 25°C. The differences are assumed to come primarily from the binders and their influences on the electrode architecture and kinetics.

Additional physical characterizations showed that binder D covered more active surface area on the graphite particles, resulting in higher R_{ct} of the electrodes with this binder. The porosimetry measurements also indicate that the electrodes with binder A have higher porosity, exhibiting a lower R_f. Therefore, the electrode design and architecture with binder A performs better in kinetics and has less polarization than those made with binder D.

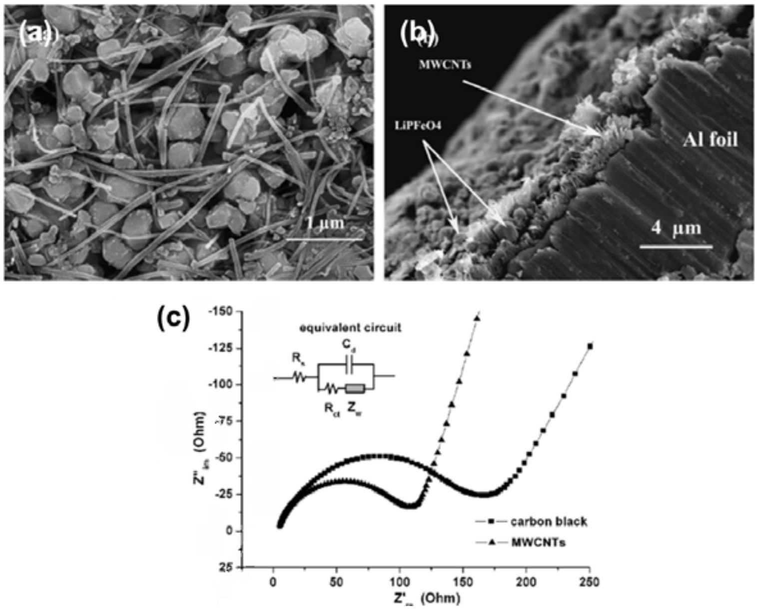


Figure 8A.14. A cell design with multi-walled carbon nanotube (MWCNT) as an additive to enhance the electronic conductivity of the positive electrode. SEM micrographs of (a) the electrode surface, (b) the cross section of the electrode showing the composite morphological structure in the electrode architecture, and (c) the change in the electrode polarization impedance [8].

Figure 8A.14 is another example of how to improve the electrode kinetics by adding electronic conductive species such as multi-walled carbon nanotubes (MWCNTs) into the electrode architecture [8]. By varying the MWCNT content in the electrode compositions, one can achieve an optimization of the kinetics for polarization. Figures (a) and (b) show a case where MWCNT was embedded in the electrode matrix. The architecture of such a structure is shown in the surface and cross section respectively. The resulting electrochemical impedance spectra are compared in Figure (c) with the one from the conventional carbon black additive. The one with MWCNT shows a much lower impedance than that with carbon black.

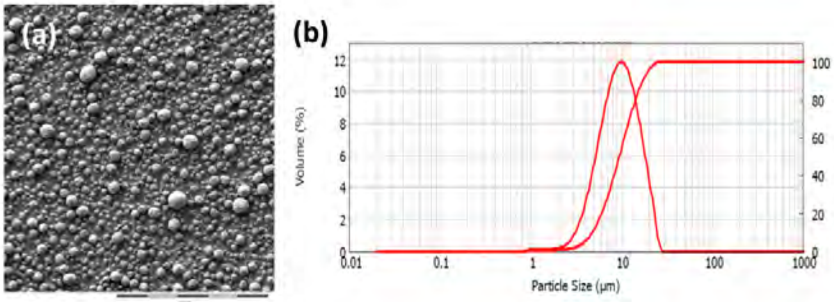


Figure 8A.15. (a) A micrograph and graphic representation of electrode architecture with graded spherical NCM particles to increase the loading density and (b) its grain size distribution determined by laser diffraction particle size analyzer [6].

Current lithium ion cell design continues to aim for high energy content. One of the critical steps toward this goal is to increase the electrode's packing (tap) density and loading. However, as packing density and loading increase, the wetting and the amount of electrolyte in the pores could be decreased, making electrode kinetic worse and polarization higher than prior designs. In addition, it is likely that the unevenness of the electrolyte distribution, polarization, and thus current distribution might create various degrees and types of parasitic reactions from one location to another, including excessive de-intercalation in the positive electrode and lithium plating on the negative. Figure 8A.15(a) shows an SEM micrograph of an electrode design with unique architecture that consists of graded particle sizes in a distribution that increases the packing and loading density of the NCM in the positive electrode [6]. The accompanied graphic representation illustrates such a design. Figure (b) is a graph showing the particle size distribution determined by laser diffraction particle size analyzer. Through careful engineering and characterization, a proper electrode design and architecture could achieve the desired kinetics and minimize polarization, while retaining high packing and loading density to provide high energy content.

8A.3.2.3 Cell design and engineering for polarization

There are additional engineering considerations beyond materials and electrodes aspects. Cell balance as mentioned previously is also critical. These balancing practices include two electrodes and the electrolyte, and not only thermodynamic stability but also kinetic compatibility, to achieve minimal polarization.

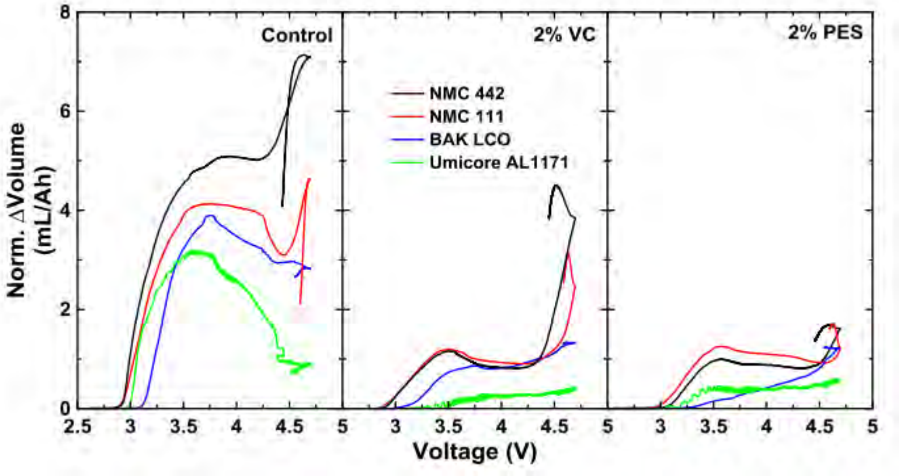


Figure 8A.16. The amount of gas evolution from various positive electrode materials in the electrolytes with VC and PES additive [9].

Figure 8A.16 is an example to demonstrate some aspects on gassing issues that are considered safety hazards [9]. Engineering to achieve minimal gassing is important to address safety concerns. In this example the amount of gas is measured by a method employing the Archimedes' principle, i.e. the volume of the gas in a cell is determined by the amount of water it displaces in a water bath. The experiments were conducted on a few positive electrode materials in a similar cell configuration. In the figure, the amount of gas generation as a function of cell voltage and the amount of vinylene carbonate (VC) or prop-1-ene-1,3-sultone (PES) additives was measured to assess the effects. Similar work on electrolyte additives for gassing mitigation and heat generation can be found in Refs. [10],[11].

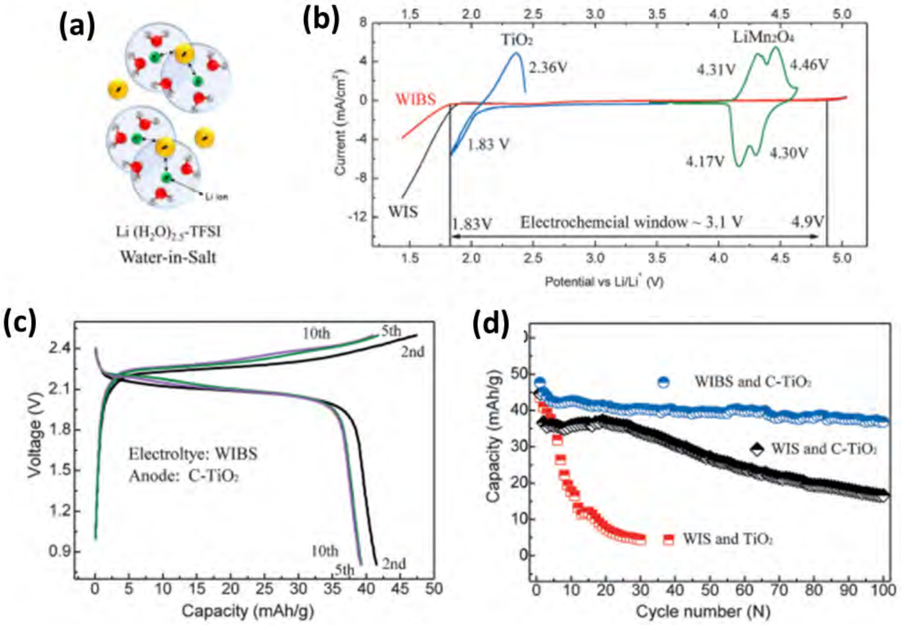
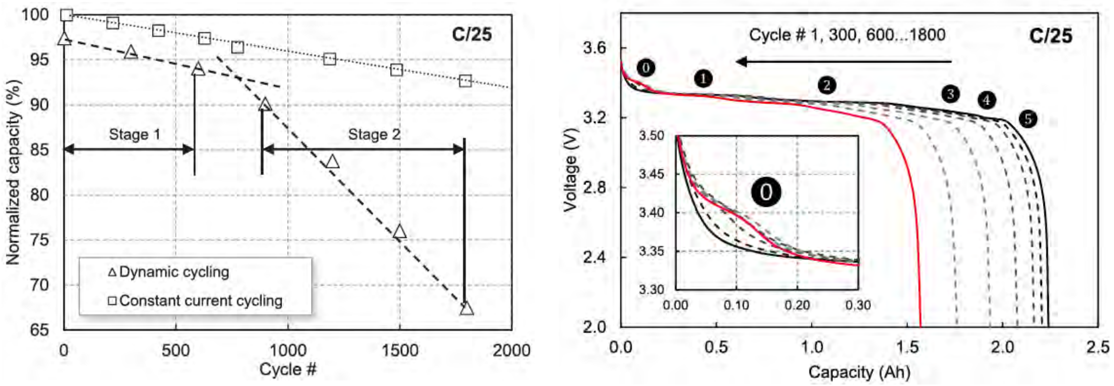


Figure 8A.17. (a) Schematic to explain the concept of “water-in-salt” and its implication on the impact of the electrolyte. (b) The cyclic voltammetric (CV) results, (c) charge and discharge profiles, and (d) charge retention curves from cells made of LTO and LMO and the “water-in-salt” electrolyte [12][13].

Besides electrolyte additives, it is possible to alter the electrolyte composition, structure and property completely to produce safer electrolyte concepts. Figure 8A.17 depicts a new concept of using “water-in-salt” electrolytes, similar to ionic liquids, to construct a new family of electrolytes and chemistry from pure organic or aqueous systems to a concentrated electrolyte type and enable moderate energy storage devices that compromise energy content for safe operation in trade-offs. More details on these concepts should refer to work reported in Refs. [12],[13].

8A.3.2.4 Aging and degradation under polarization

Cell aging and degradation could have thermodynamic origins, but also kinetic attributes. The uncertainty in these attributes from the kinetic aspects makes the risk assessment for safety very difficult to handle. This difficulty is probably the most disturbing one in the battery management. The central issue is the difficulty in establishing the baseline for comparison in order to quantify the effect and its deviation from a norm. To exemplify this statement, we may use the capacity retention as an example for discussion. The capacity is often used as the index for defining the state of the battery. This is how we used to understand state of charge (SOC) and state of health (SOH). Although it is possible to measure the capacity accurately enough to interpret the SOC for a battery, upon aging and degradation it is often challenging to determine what capacity is a reasonable expectation, and what is out of bound. On top of that, there is variability that spreads over time with aging and degradation. In addition, degradation is not a monotonic process that can be predicted with ease. Often, more than one mechanism could underpin the aging process. These mechanisms also could be subject to various degrees of response to the aging condition, thus resulting in different degrees of degradation, including capacity [14]. These stress factors underscore the spread of the variations in capacity retention over aging. Without clear understanding of these relationships, empirical correlations could be erroneous in predicting SOC and SOH [15]. To understand such underpinning mechanisms that cause capacity fade, *in situ*, non-destructive characterization tools need to be developed in order to quantify these effects. It is also critical to realize that not just capacity, but also many other factors, including mechanical and electrical impacts could alter the cell balance to make the cell unsafe.



(a) (b)

Figure 8A.18. (a) Different rates in cell capacity loss due to kinetic attributes created in dynamic cycling at variable rates versus constant current cycling duty schedules in commercial graphite || LFP cells. (b) Such attributes could cause lithium plating as shown by the additional features (⓿) observed in the discharging curves with cycling [16].

Figure 8A.18 is an example showing the capacity loss in graphite || $LiFePO_4$ commercial cells cycled under a dynamic stress test (DST) driving schedule [16]. The capacity loss is determined by actual capacity variations measured at C/25 rate in the reference performance tests (RPTs) and normalized to the initial capacity measured at the same rate. Figure (a) shows that the capacity loss follows a two-stage process in fading. In the first stage, up to about 600 deep charge-discharge cycles, the capacity loss follows a linear fashion at a fade rate of about 0.4% per 100 cycles. This fade rate is similar to those obtained in constant current cycling with various charge-discharge regimes, including typical constant current (CC)-constant voltage (CV) charging with different C rates in discharging or even multi-step fast charging and 4C discharge in each cycle [17]. During the second stage of fading, a much higher fade rate was observed after 900 cycles. This fade rate is about four times higher than the one in the first stage, attributed to lithium plating as suggested in Figure (b), where the discharge curves showed a distinct shoulder (⓿) above 3.35 V in the beginning part of the discharge regime. The fading mechanism for the first stage is due to primarily the loss of lithium inventory (LLI) and additional contributions from the loss of active material (LAM) in the negative electrode. In the second stage, lithium plating is the main factor that accelerates the fade.

This example depicts a few important aspects regarding capacity fade and its implication to safety concerns. First, the cell capacity fade does follow a fairly established mechanism of LLI and LAM in this type of LFP cells, and in this case disregarding the duty schedules as long as the operation is faithfully within the specified envelope of operating conditions. This relationship in fading can be easily established by the test results obtained from the experiments conducted in the laboratory and proper regression methods [15]. However, in the DST cycles some of high power pulses that emulate regenerative breaking could cause unexpected, progressive, incidental harsh operating conditions that operate the battery outside the normal operating envelope. These incidents triggered lithium plating when the cell ages and degrades. The severity of capacity fade grows with the extent of these lithium-plating incidents through aging, as shown by the more severe loss of capacity in the second stage than in the first. This situation depicts that the traditional empirical approach could fail to predict and to manage such anomalies, when the root cause and the underlying mechanism could not be analyzed properly and quantitatively.

Through this example, a non-invasive, operando technique is also illustrated to permit a possible identification and quantification of lithium plating to interrogate the cell to gain more insightful information in the analysis to achieve the ability of monitoring the condition of the cell [16]. This method is shown in Figure 8A.19, in which an incremental capacity (dQ/dV) analysis is used to identify the occurrence and amount of lithium plating. The incremental capacity analysis has been used in literature for more than two decades to study electrode materials in lithium-ion cells [18]. However, only recently more accurate analyses on cell degradation are being applied to understand and quantify cell degradation mechanisms and the associated effects in the cell [19][20]. In this particular case of study, two dQ/dV curves determined at C/25 were shown to reveal the differences and transitions from the initial state to the state at cycle 1800, where significant lithium plating can be identified by the presence of peak ⓿ and the associated changes in the other peaks (❶-❺) that showed intensity reductions.

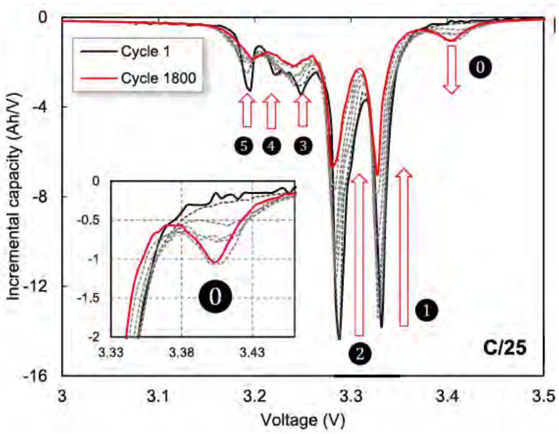


Figure 8A.19. Incremental capacity (dQ/dV) analysis used to identify and quantify lithium plating and its extent in aged cells that experience severe capacity degradation due to lithium plating.

Microscopic methods are another useful characterization tools to study materials, electrodes, and cells under aging conditions. These tools range from photographic cameras, optical microscopes, SEMs to high-resolution TEMs, and their uses depend on the objects and types of information needed for the study.

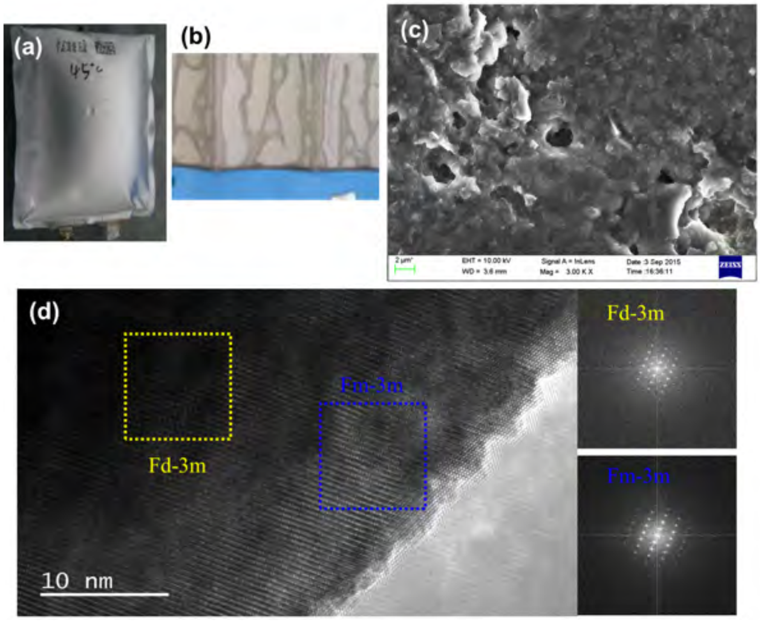


Figure 8A.20. Microscopic images obtained in the study of a graphite || NCM cell cycled at 60°C: (a) exterior inspection of the gassing condition, (b) lithium plating on the negative electrode surface, (c) SEM micrograph of morphology of the negative electrode, and (d) HRTEM image of the crystal structure near the surface of the positive electrode, including diffraction pattern changes at different micro-domains of the particle.

Figure 8A.20 shows a case study of a graphite || NCM cell going through cycling at 60°C. In Figure (a), the photo image shows the gassing condition of the cell after cycling. In Figure (b), the photograph shows the evidence of lithium plating on the negative electrode surface. In Figure (c), the SEM micrograph shows the SEI layer formation on the surface of the particles at the negative electrode. In Figure (d), the high-resolution TEM shows the crystal structure changes near the surface of the positive electrode particle. At different regions of the micro-domains in the particle, some phase transformations to spinel-like and rock salt structures can be identified by the change in electron diffraction patterns. These observations indicate the phenomena associated with aging and cell degradation. Both the lithium plating and lattice structure changes can reduce the amount of usable active materials, including reactive lithium; thus, change the cell balance. The cell imbalance could further worsen the degradation, induce overcharging and lithium plating, and directly or indirectly lead to safety concerns.

Although the imagery observations are direct evidence of possible failure modes, one of the drawbacks is the difficulty in making quantitative correlations with other physical or chemical characterizations, including the electrochemical measurements to quantify cell degradation. Such disconnects make the risk and safety assessments on the condition of the cell much less reliable and useful. How to make these different pieces of information integrated into a quantifiable platform remains a great challenge for safety engineers. Developing intermediate tools in analysis is a critical task for safety design and battery management.

8A.3.3Cell design metrics

As a final note, it is important to remember that the thermodynamic properties of materials and the associated electrochemical aspects are rather independent of cell format, form factors, geometry and shape, size and physical variations. The kinetic properties, however, are quite dependent on the above. When delivering power under polarization, only cell kinetics matters. We should be mindful that the cell manufacturing technology and operating control are not sophisticated enough to manage the kinetic aspects in sufficient precision and accuracy to allow accurate safety control, management and prevention with high resolution. This has become more and more challenging when the high energy and high power designs are desired, yet the diagnostic and prognostic capability is lacking behind. To allow such high energy and high power designs, the engineers are pushing the chemical and physical limits in the design metrics (e.g. thinning the thickness of the separator, while increasing the thickness of the electrode and reducing the porosity), whereas the capability to handle safety issues lacks the needed competency. The quality of reliability and safety assessment and risk management needs to be improved significantly.

8A.4 Cell packaging, battery management, and abuse prevention

8A.4.1Cell fabrication, quality control and packaging

Cell fabrication is a complicated process. A semi-automated process starts from the materials preparation to control the active material composition, particle size and its distribution, homogeneity in the chemical, mechanical and physical properties; followed by slurry mixing, coating, compressing/calendaring, and drying to obtain electrodes in a role-by-role configuration; then goes by cell assembly through series of steps with separator, taps, cutting/slitting, packaging into the containment casing, electrolyte filling, degassing, sealing, cell formation, aging, grading, final inspection before the cells are ready for shipping or making into module assembly. There are a number of control points for quality control and quality assurance by physical inspection, fault detection, and testing. There are also precaution steps to address possible faults in the manufacturing processes, such as foreign particle contaminations, electrode and separator misalignment, welding flaws, inadequate humidity control, formations of burrs, fraying of edges, blisters, uneven wetting of electrolyte in the porous electrodes, etc. Figure 8A.21 is a schematic to illustrate the complicated cell fabrication process in making a lithium ion cell. The key point to be emphasized here is that the quality control and quality assurance (QC/QA) involved in the process is quite extraordinarily complex, mundane and tedious, requiring precision and accuracy to achieve the quality to ensure the cells perform with good consistency, durability, reliability and safety. How to quantify the necessary precision and accuracy remains a challenge to date, not to mention the conduct of FMEA to define the effects quantitatively.

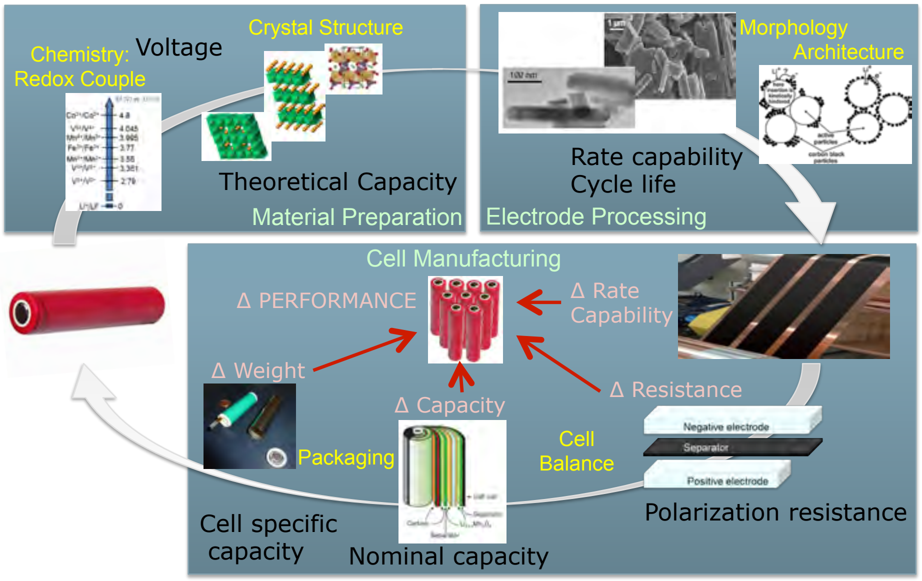


Figure 8A.21. Schematic that illustrates the lithium-ion cell fabrication process, which is prone to creating cell variability due to the complexity in process control and quality assurance in manufacturing.

8A.4.2Safety devices

Besides safe design in cell internal configurations, additional protection devices to prevent or minimize abuses are commonly used in the safeguard of the cell or battery. Electrical fuses are one of the examples that often used in the external circuit to prevent electrical short-generated over-current conditions to propagate in the modules or packs and to lead to additional damages and escalation of safety risks. Another over-current protection is to use a positive temperature coefficient (PTC) device, of which the resistance of the device will increase with temperature (due to increase in joule heating by the over-current) to reduce current flow. The difference is: when fuses are tripped, they need to be replaced; yet, PTC devices can be reset. Another protection device often used is current interrupt device (CID), which is commonly collated with gas venting mechanism to disable the cell when high pressure, high temperature and/or high current may trigger safety protection by venting the gas generated from the cell and trip the current path to prevent further propagation of the unsafe event. Figure 8A.22 shows two schematics of a typical 18650 cell with top cover cap that contains PTC, CID and gas vent in the crimped can [21][22].

Figure 8A.22. Schematics to show a typical 18650 cell with positive temperature coefficient (PTC) thermistor, current interrupt device (CID), and a gas vent that are used to provide safeguard for a lithium-ion battery [21][22].

These protection devices are invented and designed for common 18650 cells, which are quite matured in production today; so, the devices are built into the cell design and manufacturing process. For larger format prismatic and pouch cells with higher capacity for electric vehicle or energy storage applications, these protection devices might not work as mature as anticipated and need to be re-engineered to scale to the proper design in order to function well. Sometimes, these devices might become cost-prohibitive for larger format batteries, if they are not standardized for mass production in volume. In such cases, alternative solutions with battery management systems might be considered with additional care in place to ensure safety during the operation of the systems.

8A.4.3Battery management

Even though this chapter should focus on cell safety issues and engineering designs to mitigate or prevent safety incidents, it is still relevant to discuss the cell packaging, battery management, and abuse prevention in conjunction with the cell safety concerns. Here the discussions shall focus on how cell variability percolates into the pack, how battery management and control could produce stress on cells in the pack, and how system abuses could trigger cell imbalance and worsen cell durability, reliability and safety.

A battery system could create hazards to compromise the integrity of the cells in the system. Inadequate packaging, system managements (mechanical, electrical and thermal), and control (e.g. unreliable algorithms, accuracy, precision, noise) all can produce abusive conditions to harm the cells. The intricacy and severity of such potential interferences and damages might not be easy to detect. In the worst scenario, the system mishaps might not be sufficiently investigated, and they may disarm the safety measures built into the cells.

A common negligence of the cell variability and its implication to cell reliability and safety is a great concern. There is little discussion of this aspect in the literature. There is almost no strategy or methodology to deal with this problem in a quantitative manner. Most of the safety engineers often ignore the sensitivity of the cause-and-consequence relationship in the battery aging and degradation, which could not be easily determined and managed through statistical analyses and reliability tests. One of the obstacles is the interrelationship among the couplings of thermal, mechanical, electrical and chemical properties of the battery system and the cells.

An interesting discussion on cell variability and understanding its origins via analytical assessments can be found in Ref. [23]. In this article, the authors use a batch of 100 cells through careful testing and analysis to relate and understand the distribution of the physical parameters and the performance characteristics of the batteries. A key element in the context of analyzing the cell variability is the quantitative clarification of the cause-and-consequence relationship beyond the statistical analysis and providing some physical meaning of such a relationship.

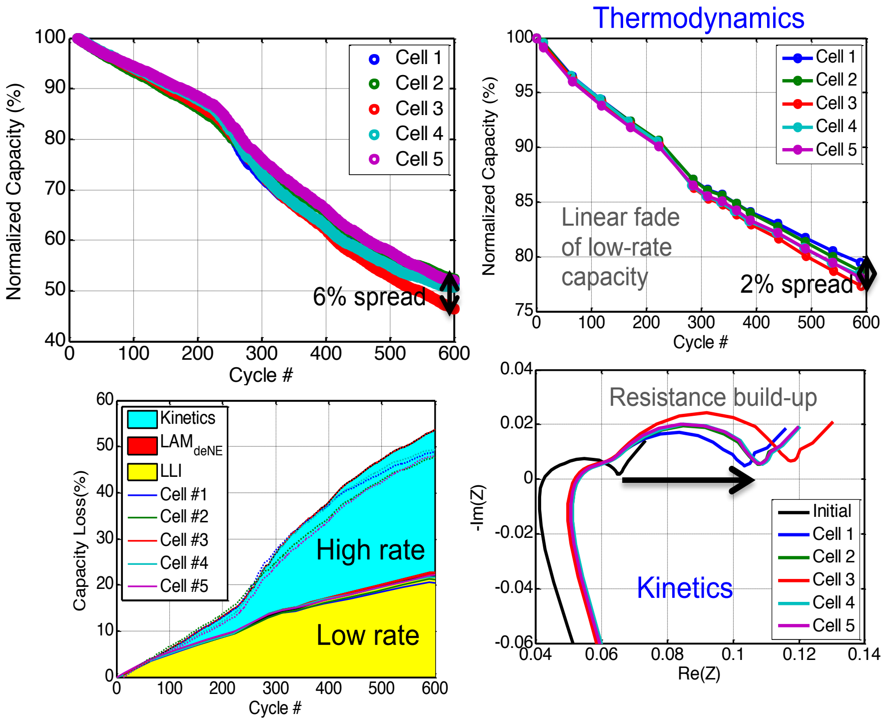


Figure 8A.23. A cell variability analysis on five cells that experienced cycle aging and capacity variations. Tracing such variations could reveal the complexity of the cell variations in the aging process [24].

This cause-and-consequence relationship will continue to change as the cells age and degrade in performance. The further analysis of such changes in the cause-and-consequence relationship is more complicated, but it is feasible [24]. Figure 8A.23 is an example of how to trace such a relationship though cell aging. Here five commercial cells of high quality were examined for their capacity fade over a cycle aging experiment. The charge retention shows that the five cells had about 6% of spread in capacity after 600 cycles of aging. Using a careful dQ/dV analysis, the cell chemical balance due to materials losses can be extracted from the dQ/dV data and proper analysis.

Such materials losses in the cell balance contributed to about 2% of spread in the variations. The analysis of the electrochemical impedance spectroscopic data further suggests that the kinetic contributions to the spread in the variations are about 4%. This example delivers a very important message. Proper understanding of such cause-and-consequence scenarios is very helpful in the risk analysis and battery management because this methodology shall allow us to continue monitor the system and understand how to trace the baseline performance changes from the causes. Such an analytic basis shall constitute a reliable diagnostic and prognostic capability to identify outliers and anomalies.

It is also interesting to point out that in this particular case, the initial degradation in capacity fade was caused by loss of lithium inventory up to about 200 cycles. A secondary fading mechanism emerged then, which was likely a kinetic origin that caused additional fading to take place in addition to the loss of lithium inventory. This marked the transition to a second stage of fading and the capacity quickly faded to below 80%, while the kinetic fading continued to take a toll and widen the variations. The lesson learned is that an assumption of capacity fade under a monotonic process does not prevail well to predict life. Not knowing the cause-and-consequence relationship quantitatively, projection of fading process for life prediction could be misguided. Testing and test results provide certain guidance based on empirical correlation, but its accuracy and confidence level might not be sufficiently defined in field operation when the operating conditions are less controlled. Especially, when operating conditions continue to evolve and change, the predictability based on the empirical results might become vulnerable. The mechanistic understanding of cause-and-consequence might provide a better solution to address this issue.

An interesting approach based on mechanistic diagnostics to achieve prognostic prediction is introduced in Ref. [25]. Figure 8A.24 shows the schematic that depicts the approach of using electrode level models to emulate cell performance with degradation mechanisms built into the scenarios for capacity fade prediction. The unique capabilities lie on the ability to incorporate metrics in electrode design and degradation as a function of thermodynamic and kinetic attributes so their impacts on cell level balance can be projected. This level of granularity is very useful in projecting cause-and-consequence results to understand how a fading mechanism impacts the cell performance. By matching the projection and the test results, this modeling tool can be used as a diagnostic method to identify possible capacity fade mechanisms and their degree of impact in a quantitative manner, which forms the basis for prognostics. The same approach can be extended to estimating the degree of impacts on reliability and safety and to allow better quantification of abuse and its impacts on the safety to develop better strategy for improved tolerance and resilience.

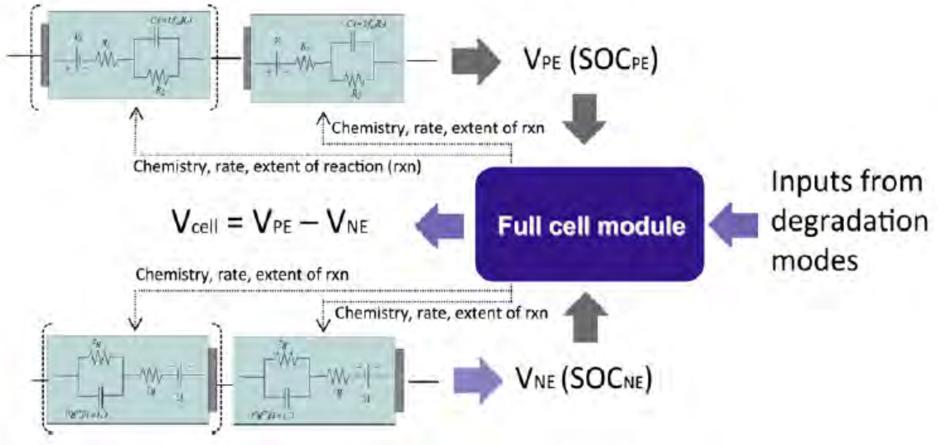


Figure 8A.24. Schematic showing a mechanistic modeling approach for a battery diagnostic that is capable of analyzing electrode level failure mechanisms to understand their impacts on cell performance for prognostic prediction [25].

8A.5 Quality control, storage, maintenance and repair

The ability to conduct cell and system level diagnostics and prognostics is a critical element to achieve better safety and safety measures. On the cell manufacturing side, diagnostics can help quality control and quality assurance. With improvements on cell monitoring sensory and accuracy, the assessments of cell degradation, anomaly, risk and the degree of compromise could also be well established for safety measure and control. These improvements can drastically reduce the uncertainty on the effects from storage. The improvements can also facilitate the scheduling of maintenance and repairs with reduced hazards.

The diagnostics can further allow the assessments of effects from environmental impacts. Thermal management of battery systems is an important topic in this regard. Figure 8A.25(a) is an example of the thermal gradient distributions in an interior of a battery pack [26]. Although temperature mapping might be achievable by sensory and instrumentation, or even a numerical (3-D) model could be used to simulate such distributions (Figure 8A.25(b)), fidelity and accuracy in the prediction of the temperature and its distribution remain as issues of concerns. More discussions on the thermal management and the systems can also be found in Chapter 8B “Managing of risk by battery manufacturers.”

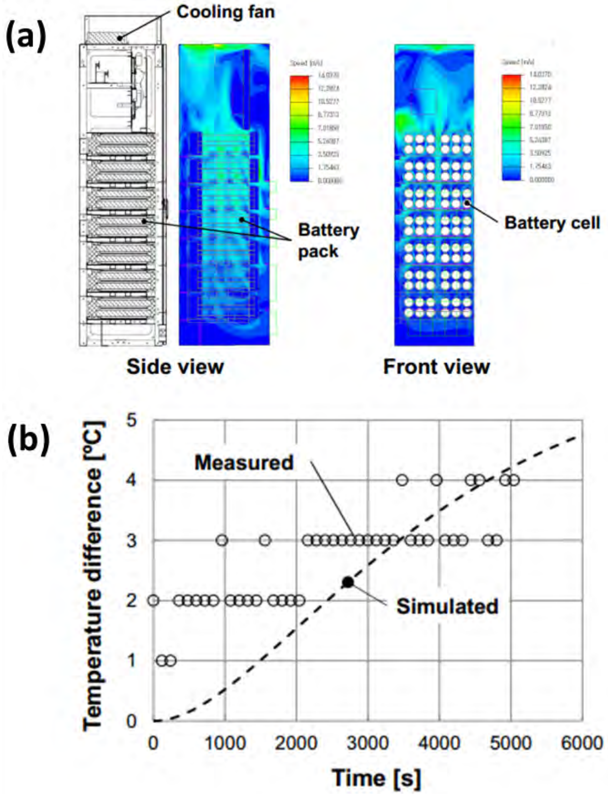


Figure 8A.25. (a) Temperature mapping of a battery pack showing the thermal gradients and distributions in the interior of the pack. (b) Temperature measured and simulated in an energy storage battery rack undergoing 1 MW of charging discharging cycles [26].

The magnitude of the impact from the thermal effects on cell degradation and defect in performance are often difficult to assess and predict. Thus, the propensity of early failure and thermal runaway might not be easy to quantify. One should be mindful that a more severe degradation could also generate more heat due to the degradation. This coupled effect could undermine the original prediction of failure and lead to unexpected premature failure.

8A.6 Failure detection, diagnosis and prognosis

Earlier failure detection is an important step for safety measures, if proper diagnostics and prognostics can be established to predict reliability. To achieve so, new techniques to allow proper interpretation of signatures that could implicate cell failure are highly desired. Such capabilities include physical and chemical detections, models and simulations, and intelligent algorithms to determine the risks.

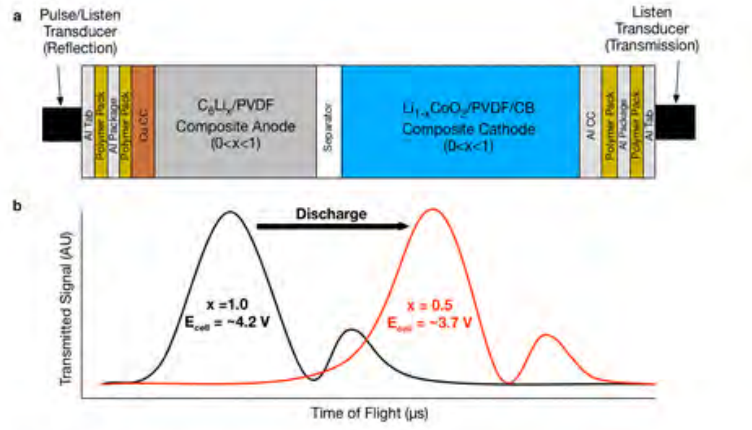


Figure 8A.26. An *in operando* electrochemical-acoustic time-of-flight analysis technique that shows correlation of physical dynamics within a cell as a function of states of charge and health [27].

Figure 8A.26 shows an example of a unique electrochemical-acoustic time-of-flight analysis technique that can perform *in situ, operando* probing of the state of the cell [27]. As a cell going through electrochemical reaction, the extent of the reaction will cause mass redistributions and other physical changes that can be sensed by transmission of acoustic waves. By analyzing the time-of-flight data, in which changes in the acoustic wave responses from the cell interior can be used to interpret how much changes have occurred in the cell. Such correlations could be useful to monitor the interior variations in density, porosity, and tortuosity of certain regions in the cell and indirectly implying how such changes can impact the safety aspects of the cell. Instances of safety concerns such as lithium plating have been observed and reported using this technique; thus, it can be used as a non-invasive probe for safety during battery operation. Although the sensitivity, accuracy and resolution, the interpretation of the data analysis, and validation of such interpretations should be further developed to make this technique useful for cell diagnosis and prognosis, innovation of such and similar approaches is important in the future for battery safety management, abuse mitigation and failure and safety hazard prevention.

8A.6.1Untra high precision charger (UHPC)

The charge retention and cycle life of a cell is determined by the influence of thermodynamics and kinetics. In the thermodynamic aspect, the capacity loss could come from either the loss of active materials in the electrodes or the loss of lithium inventory in the electrodes and/or the electrolyte. To minimize the loss, a possible solution is to have a tight charging control to prevent such losses. Ultra high precision charger (UHPC) as an electrochemical workstation to control the formation and charging process is a trendy practice [28]. UHPC could be used in the initial determination of the charging protocols. By carefully measuring the amount of charge in the constant voltage (CV) step in a typical CC-CV charging protocol (charge slippage), the amount of active materials loss could be derived and estimated. By using coulombic efficiency, the lithium inventory loss could be estimated as well.

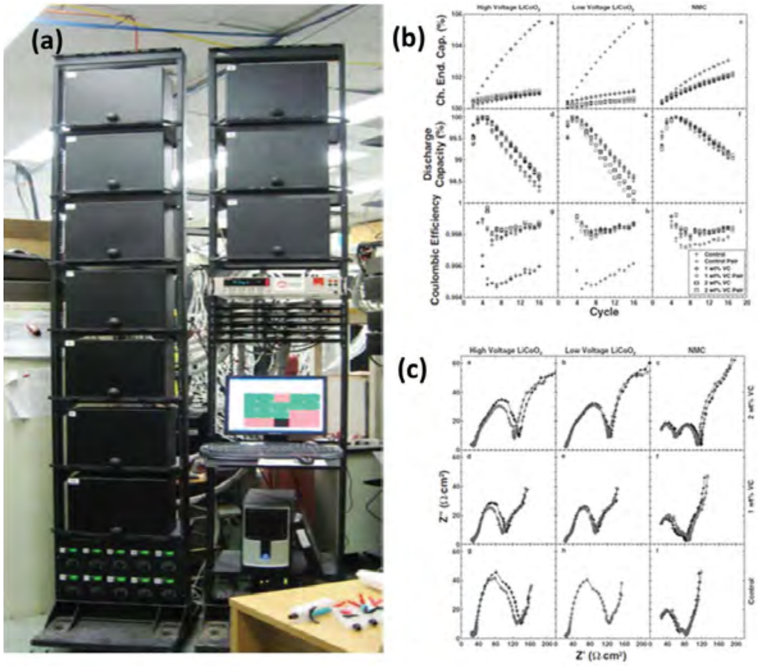


Figure 8A.27. (a) An ultra high precision charger (UHPC) that can be used to control formation and charging process [28]. By measuring (b) the amount of charge in the constant voltage (CV) step in a typical CC-CV charging protocol, the coulombic efficiency, and (c) the information derived from electrochemical impedance spectroscopic technique, an optimal charging process can be formulated [29].

To understand the kinetic effects, the electrochemical impedance spectroscopic (EIS) techniques can be used to analyze the impact of the stress factors on the cell performance in order to determine the degree of influences. By combining the charge slippage, coulombic efficiency, and the EIS analysis, most of the thermodynamic and kinetic effects can be estimated to provide more accurate prediction of charge retention and cycle life or calendar life. Such an accurate life prediction is critical to estimate the state of health of the cell and its impact on the cell reliability. In conjunction with dQ/dV analysis during the discharge regime, the cell balance, degradation mechanism, and the degree of cell imbalance could be estimated and the implication of such cell imbalance to safety consequences could also be assessed to infer how much tolerance might be still available to weather abusive conditions. Such a measure is an ultimate objective in safety management.

Figure 8A.27 is an example showing an UHPC system [28] that can perform the task of determining charge slippage, coulombic efficiency, and EIS parameters to optimze charging protocols and predict cycle life of a cell design and quality, as reported by J. R. Dahn and his co-workers on how to assess the function of electrolytes and their impacts on cell performance and cycle life. For instance, a case study in Refs. [29] showed that the content of vinylene carbonate (VC) can have implication on cycle life of LCO and NMC. By using different amounts of VC as an additive in the electrolyte (0-2 wt%), the impacts on the cycle life for LCO (with the charge cutoff voltage at 4.175 V and 4.075 V, respectively) and $LiNi_{0.42}Mn_{0.42}Co_{0.16}O_2$ in wound prismatic cells in which mesocarbon microbeads (MCMB) was used as the negative electrode could be studied and the results can aid the validation of the understanding and quantification of the benefits of the additive. The final goal is to enhance the cycle life of the cell design.

8A.7 Conclusions

To address battery durability, reliability and safety quantitatively is very challenging with the engineering capabilities we have to date. A major takeaway is that statistical analysis without properly addressing the cell variability may lead to misguided performance prediction, resulting in unexpected safety events. To engineer a safe battery design, adequate failure mode and effect analysis with proper diagnostic and prognostic techniques is a future solution. This practice has to be performed quantitatively. Cause-and-consequence based mechanistic understanding needs to be established beyond statistical means in order to enable the safe design practice. There is no short cut to reliability and safety in battery designs.

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Captions for Figures and Tables

Figure 8A.1. Relationship of durability, reliability and safety in reference to abuse tolerance for a chemical system like battery.

Figure 8A.2. (a) Phase diagram of $Li(Ni_xCo_yMn_z)O_2$ (NCM) positive electrode compositions and (b) the electronic structures of $LiCO_2$ (LCO), $LiNiO_2$ (LNO), and $LiMn_2O_4$ (LMO) positive electrode materials [1].

Figure 8A.3. The rate of temperature increase as a function of temperature in several well-known positive electrode materials in 18650 cells obtained by adiabatic reaction calorimeter (ARC). This representation is used to indicate the thermal stability of electrode materials [5].

Figure 8A.4. (a) Elemental Mn and Ni distribution on the surface and core of a core-shell NCM positive electrode material. (b) The DSC results show the surface-Mn-rich core-shell material has better thermal stability than the conventional NCM-523 material [6].

Figure 8A.5. An example showing that mixing NCM with a thermally more stable $LiMn_xFe_yPO_4$ (LMFP) composition in the positive electrode could improve its safety aspect without sacrificing electrochemical performance. The SEM micrographs show (a) the electrode surface morphology (b) the cross section of the electrode architecture. (c) Charging and discharging profiles and (d) charge retention in cycle performance for the NCM base material and the NCM+LMFP composites.

Figure 8A.6. DSC results show the composite electrodes of (a) NCM+LMO and (b) NCM+$LiMn_xFe_yPO_4$ (LMFP) could exhibit better thermal stability than the base NCM material. (c) The amount of oxygen released in several compositions of NCM+LMO samples. (d) The temperature of oxygen release as a function of LMO content in the composition [7].

Figure 8A.7. Results of nail penetration experiments with cells made of (a) graphite || NCM and (b) graphite || NCM+LMFP. In each figure, the dash lines are cell voltage and solid lines are cell temperature [7].

Figure 8A.8. (a) TEM image showing the surface crystal structure changes in a cell with graphite || NCM under a condition of cell over-balance (negative electrode is more than desired). (b) Lithium plating shown on the negative electrode due to cell under-balance (negative electrode is less than desired).

Figure 8A.9. Distribution of capacity (a) among graphite || LFP cells of different lots that use various batches of LFP material and (b) among different LFP electrodes in similar cells of the same batch. [COV: Coefficient of Variation]

Figure 8A.10. The (a) thickness, (b) ac impedance, (c) internal pressure of the cell, and (d) surface morphology changes of the positive electrode in nominal graphite || NCM cells that undergo calendar aging at an elevated temperature.

Figure 8A.11. Electrode architecture and materials stability demonstrated by an NCM-based electrode design and architecture. Micrographs of the NCM electrode: (a) after the cold press and (b) after cycling for comparison. (c) Graphical mechanistic explanation of the particle pulverization leading to swelling of the electrode upon cycling.

Figure 8A.12. (a) The charging profiles of a nominal graphite || NCM cell under charging at different rates. (b) The cell surface temperature variations and (c) the visual evidence of Li plating on the surface of the negative electrode.

Figure 8A.13. (a) The ac impedance of graphite negative electrodes prepared with different binders. (b) Different attributes to the cell impedance were analyzed for comparison of the impacts from the binders. The experiments were performed at 25°C with a symmetric cell configuration.

Figure 8A.14. A cell design with multi-walled carbon nanotube (MWCNT) as an additive to enhance the electronic conductivity of the positive electrode. SEM micrographs of (a) the electrode surface, (b) the cross section of the electrode showing the composite morphological structure in the electrode architecture, and (c) the change in the electrode polarization impedance [8].

Figure 8A.15. (a) A micrograph and graphic representation of electrode architecture with graded spherical NCM particles to increase the loading density and (b) its grain size distribution determined by laser diffraction particle size analyzer [6].

Figure 8A.16. The amount of gas evolution from various positive electrode materials in the electrolytes with VC and PES additive [9].

Figure 8A.17. (a) Schematic to explain the concept of “water-in-salt” and its implication on the impact of the electrolyte. (b) The cyclic voltammetric (CV) results, (c) charge and discharge profiles, and (d) charge retention curves from cells made of LTO and LMO and the “water-in-salt” electrolyte [12][13].

Figure 8A.18. (a) Different rates in cell capacity loss due to kinetic attributes created in dynamic cycling at variable rates versus constant current cycling duty schedules in commercial graphite || LFP cells. (b) Such attributes could cause lithium plating as shown by the additional features (⓿) observed in the discharging curves with cycling [16].

Figure 8A.19. Incremental capacity (dQ/dV) analysis used to identify and quantify lithium plating and its extent in aged cells that experience severe capacity degradation due to lithium plating.

Figure 8A.20. Microscopic images obtained in the study of a graphite || NCM cell cycled at 60°C: (a) exterior inspection of the gassing condition, (b) lithium plating on the negative electrode surface, (c) SEM micrograph of morphology of the negative electrode, and (d) HRTEM image of the crystal structure near the surface of the positive electrode, including diffraction pattern changes at different micro-domains of the particle.

Figure 8A.21. Schematic that illustrates the lithium-ion cell fabrication process, which is prone to creating cell variability due to the complexity in process control and quality assurance in manufacturing.

Figure 8A.22. Schematics to show a typical 18650 cell with positive temperature coefficient (PTC) thermistor, current interrupt device (CID), and a gas vent that are used to provide safeguard for a lithium-ion battery [21][22].

Figure 8A.23. A cell variability analysis on five cells that experienced cycle aging and capacity variations. Tracing such variations could reveal the complexity of the cell variations in the aging process [24].

Figure 8A.24. Schematic showing a mechanistic modeling approach for a battery diagnostic that is capable of analyzing electrode level failure mechanisms to understand their impacts on cell performance for prognostic prediction [25].

Figure 8A.25. (a) Temperature mapping of a battery pack showing the thermal gradients and distributions in the interior of the pack. (b) Temperature measured and simulated in an energy storage battery rack undergoing 1 MW of charging discharging cycles [26].

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